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Heterogeneous catalytic 2,4,6-trichlorophenol degradation at hemin–acrylic copolymer

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ABSTRACT

The synthesis, characterization and evaluation of the catalytic properties of a hemin–methacrylamide–ethylene glycol dimethacrylate copolymer are described. This polymer catalyzes the oxidative dechlorination of 2,4,6-trichlorophenol (TCP) in the presence of hydrogen peroxide, yielding 2,6-dichloro-1,4-benzoquinone as the main reaction product. This low-cost material allows the complete removal of TCP from water at concentration level of 20 mg L^{-1} in less than 30 min.

1. Introduction

2,4,6-Trichlorophenol (TCP) and other chlorophenols constitute a group of priority pollutants listed by the US Environmental Protection Agency (EPA) in the Clean Water Act and by the European Union (EU) in the Decision 2455/2001/EC. They have been employed in the manufacturing of herbicides, fungicides, pesticides, insecticides, pharmaceuticals and dyes. Chlorophenols may be also generated as by-products during waste incineration, the bleaching of pulp with chlorine and the dechlorination of drinking water. They can be found in ground waters, wastewaters and soils [1]. Their toxicity and persistence in the environment increase with the degree of chlorine substitution. In particular, TCP causes respiratory effects from cough to serious pulmonary lesions.

Due to their high toxicity, carcinogenic properties and persistence in the environment, several strategies have been followed to remove them from the environment. Conventional methods include thermal, chemical and biological treatments [2].

The biological methods are remarkable because of the environmental availability and the low cost of the microorganisms, which live in muds, sludges and sewages. However, microorganisms require specific conditions to carry out their degradation reactions by reductive dehalogenation route in anaerobic conditions or by an oxidative pathway [3]. These factors include pH value, number of microbes, viscosity [4], temperature, oxygen, water and nutrients availability, and the presence of products from the decomposition of roots. On the other hand, the majority of chlorophenols are poisonous to microorganisms, so the direct use of biological treatment is not effective in many cases. Sometimes an enzymatic pre-treatment is advised before the subsequent microbiological step. Moreover, depending on the biocatalyst, the reaction conditions and the chlorophenol characteristics, the sole use of enzymes could result in the formation of polymeric products that could be removed by filtration [5,6] or even in the complete degradation to CO_2 and H_2O. Some enzymes (summarized in Table 1) have been used to degrade a wide variety of chlorophenols and even 4-fluorophenol.

As it can be seen, the enzymes belong to the heme-peroxidases and P450 cytochrome families, whose structures consist on aminoacidic chains surrounding the active site, where the heme molecule is housed. Therefore, heme-like iron catalysts involving planar coordination of four nitrogen donor atoms may be adequate to activate hydrogen peroxide toward chlorophenols oxidation. Some of the reagents explored for homogeneus catalytic degradation involve porphyrins and phthalocyanines with diverse metal centres or even without metal atoms as catalysts, as summarized in Table 2.

Abbreviations: MA, methacrylamide; EGDMA, ethileneglycoldimethacrylate; AIBN, 2,2′-azo-bis-(isobutyronitrile); DMSO, dimethylsulfoxide; 2-CP, 2-chlorophenol; 3-CP, 3-chlorophenol; 4-CP, 4-chlorophenol; 2,4-DCP, 2,4-dichlorophenol; 2,6-DCP, 2,6-dichlorophenol; TCP, 2,4,6-trichlorophenol; 2,3,5,6-TeCP, 2,3,5,6-tetrachlorophenol; PCP, pentachlorophenol; 4-FP, 4-fluorophenol; DCQ, 2,6-dichloro-1,4-benzoquinone.

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Table 1
Enzymatic degradation of halogenated phenols.

Enzyme	Source of supply	Substrate	Reference
Chloroperoxidase (CPO)	*Caldariomyces fumago*	Phenol; TCP	[7]
		4-CP	[8]
		2,4-DCP	[9]
		2,3,5,6-TeCP, PCP	[10]
		4-FP	[5]
Laccase	*Trametes versicolor*	2-CP, 3-CP, 4-CP	[11]
		2,4-DCP; 2,6-DCP; TCP	
Lignin peroxidase (LiP)	*Phanerochaete chrysosporium*	2,4-DCP; TCP; PCP	[12,13]
Myoglobin (Mb)	*Horse heart*	TCP	[14]
Horseradish peroxidase (HRP)	*Horseradish*	2,4-DCP; TCP; PCP	[7,15,16]
Dehaloperoxidase (DHP)	*Amphitrite ornata*	TCP	[17,18]

The immobilization of the catalytic centre offers some advantages with respect to their soluble counterparts: robustness, stability, easy separation by filtration and the potential recyclability [26]. The supports on which metal complexes have been immobilized are inorganic or organic polymers. The formers are typically oxides bearing surface hydroxyl groups and the latters are consist on a suitable combination of monomers and cross-linkers that conjugate the flexibility of the matrix with the possibility to fine-tune physical properties (polarity, swell ability, morphology) of these materials.

In this work, we have synthesized an acrylic polymer with a neutral functional monomer (methacrylamide, MA) to mimic the aminoacids in the peptidic chain of the enzymes. Additionally, we have incorporated hemin, a special monomer that could act as the catalytic centre of the enzyme. The catalytic activity of the polymer has been studied toward the oxidative dehalogenation of TCP because it is often used as reference to test the efficiency of oxidative degradation methods [27].

2. Experimental

2.1. Reagents

Sodium acetate, $HClO_4$ and acetic acid were obtained from Merck. Hydrogen peroxide was purchased from Prolabo, 2,6-dichloro-1,4-benzoquinone (DCQ) was obtained from Aldrich and 2,4,6-trichlorophenol (2,4,6-TCP) from Riedel de Haën as Pestanal® standard. A stock standard solution was used to daily prepare working standard solutions by suitable dilution in a 0.01 M acetate buffer.

Fe(III)-protoporphyrin IX (Hemin) was purchased from Frontier Scientific (UK), methacrlyamide (MA) from Aldrich, 2,2′-azo-bis-(isobutyronitrile) (AIBN) from Sigma and dimethylsulfoxide (DMSO) from Fluka. All these reagents were used as received. Ethileneglycoldimethacrylate (EGDMA) was obtained from Merck and its inhibitors were removed by liquid–liquid extraction to a basic aqueous medium. Acetonitrile was purchased from J. T. Baker and Hg $(SCN)_2$ was obtained from Panreac.

All other chemicals were analytical-reagent grade. All solutions were prepared with high purity water produced by a Milli-Q purification system (Millipore).

Table 2
Degradation of halogenated phenols with porphyrins, phthalocyanines and macrocylic ligands.

Metal centre	Substrate	Oxidant	Reference
Fe	4-CP; TCP	H_2O_2, $KHSO_5$	[19–25]
Mn	TCP	H_2O_2, $KHSO_5$	[19,23]
No metal	4-CP; 2,4-DCP;TCP; PCP	H_2O_2, $KHSO_5$	[24]

2.2. Apparatus

High performance liquid chromatography (HPLC) was used to separate and analyze the products of the heterogeneous oxidation of TCP catalyzed by the polymer and carried out at pH 3.0. The HPLC equipment used was a gradient Shimadzu 20A system fitted with a SPD-20MA diode array detector and a Rheodyne 7725i rotating valve with a 20 μL loop. A 150 mm Pinnacle C18 column (5 μm particle diameter and 4.6 mm I.D.) supplied by Teknokroma (Spain) was used. Data analysis was carried out with Shimadzu LC Solution software. The chromatographic separation was performed with a mobile phase consisting of 0.05 M acetate buffer pH 3.5 (solvent A) and acetonitrile (solvent B). The gradient elution program was as follows: keeping constant 50% B for 6 min, then increasing to 90% B in 1 min and keeping constant until 9 min. Then restored to 50% B and followed by a 5 min equilibration time. The flow rate was set at 1 mL min^{-1}. The detector was set at 280 nm to detect both TCP (λ_{max} = 290 nm) and DCQ (λ_{max} = 272 nm) in a single chromatogram (retention times: 3.7 min for DCQ and 7.2 min for TCP).

Mass spectra were obtained with a high performance liquid chromatograph (HPLC 1100 Series, Agilent Technologies, Tokyo, Japan) coupled to an ion trap MS detector (LC/MSD Trap XCT Plus, Agilent Technologies, Tokyo, Japan). The chromatographic separation was performed with the same column and time programme as HPLC–UV/VIS measurements.

2.3. Synthesis of the polymer

Hemin (5 mmol), MA (25 mmol), and EGDMA (250 mmol) were dissolved in DMSO (7.5 mL) in a vial. The vial was sealed and the mixture was purged with nitrogen for 15 min. Then AIBN (240 mg) was quickly added and the mixture was purged again for 5 min. The polymerization reaction was carried out in an oven at 65 °C for 24 h. The non-polymerized hemin was removed from the polymer by Soxhlet extraction with methanol containing 15% (v/v) acetic acid until no colour was observed. The polymers were finally washed with methanol to remove the acid, crushed and sieved to obtain particles sized below 25 μm to use in batch experiments.

2.4. Characterization of the polymers

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) experiments were carried out on MEB JEOL-6100 and MET JEOL-2000 EX-II instruments, respectively. SEM specimens were prepared by dispersing a little amount of polymer on carbon tape on aluminium stubs, and coating them with gold under vacuum (Sputtering Blazers SCD 004). TEM samples were prepared by depositing few drops of a freshly prepared polymer suspension in ethanol, on a carbon coated grid, which was

subsequently air dried at room temperature before loading it into the microscope.

The absorption spectra were performed in a Lambda 20 spectrometer from PerkinElmer (USA).

To determine the iron content in the polymer 20 mg were suspended in 1 mL of $HClO_4$ 2 M and incubated with H_2O_2 15% (w/v) for 14 h under stirring. The mixture was centrifuged and the iron content in the supernatant solution was determined with a 7500ce model ICP-MS (Agilent Technologies, Tokyo, Japan). The instrument consists of an ICP source with a plasma-shielded torch, an enclosed octopole ion guide operated in RF only mode and a cuadropole mass analyzer. A continuous flow of 3.5 mL min^{-1} of helium as the reaction gas was introduced into the octopole reaction system under mass flow control through stainless steel lines, and m/z 56 was measured. The lixiviating operation was performed further for 15 min in the conditions previously described although no significant amounts of iron were found in these supernatants.

2.5. Batch kinetic assays

Degradation of TCP was carried out in small flasks (4 mL) as batch reactors with the acrylic polymer (0.5 g L^{-1}) as catalyst. Measurements were carried out at 25 °C in aqueous medium with 10% DMSO to wet the polymer. Since an excess of hydrogen peroxide over the substrate has been extensively employed in the degradation of chlorophenols [6,17], a H_2O_2 concentration of 10^{-3} M was fixed for all experiments. pH was optimized and then kinetic studies were carried out at the optimum conditions. In order to release any TCP remaining adsorbed on the polymer surface and not transformed, the synthetic material was washed with 1 mL of methanol. The resulting washing solution was added to the reaction mixture. Therefore every point in the figures of the kinetic results is accumulative.

3. Results and discussion

3.1. Characterization of the polymers

The morphology of the resulting polymer was evaluated by SEM and TEM. Fig. 1A shows the morphology of the polymer particles. The estimated average size (distance between two tangents at opposed sides of the particle profile) results in 15 μm approximately, although a dual distribution was observed (10 ± 3 μm and 20 ± 3 μm). These particles are formed of spherical substructures (Fig. 1B) with 27 ± 10 nm diameters. The rapprochement of these substructures creates pores sized 20 ± 5 nm.

Additionally, the presence of hemin in the polymer was confirmed by Absorption Spectroscopy. Fig. 1C shows the UV–VIS absorption spectrum of a DMSO polymer suspension (0.2 g L^{-1}), and the observed absorption bands (401 nm, 500 nm and 657 nm) match with a 2×10^{-3} g L^{-1} hemin standard solution. Finally, the iron content in the polymer (0.03 %) was estimated by lixiviating with hydrogen peroxide in an acidic medium and quantification of the released iron by ICP-MS.

3.2. Optimization of the reaction conditions

3.2.1. Identification of the main reaction product

The oxidation of TCP by H_2O_2 using the polymer as catalysts was followed by HPLC measurements. We let stand the TCP solution for 5 min with the synthetic polymer as catalyst, as described in Section 2.5, and then we carried out a HPLC–MS analysis of the reaction medium. The mass spectra were recorded at 3.7 and 7.2 min and exhibit m/z ratios of 176.9 and 194.9, which correspond to 2,6-dichloro1,4-benzoquinone (DCQ) and TCP,

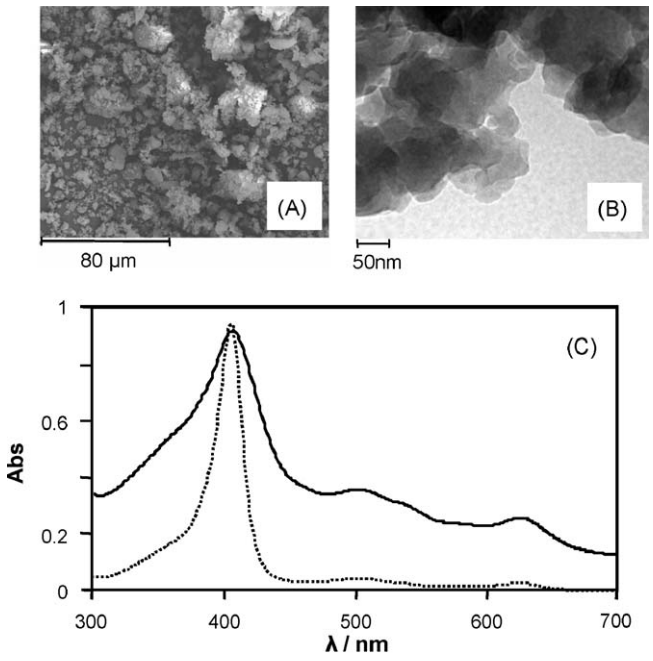
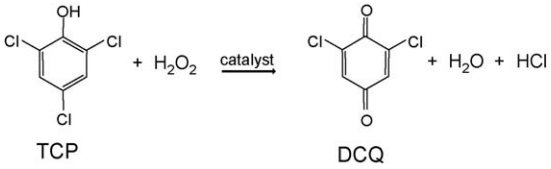


Fig. 1. SEM (A) and TEM (B) micrographs of the acrylic polymer. (C) Absorption spectra of (—) a 0.2 g L^{-1} DMSO polymer suspension and (···) a 2×10^{-3} g L^{-1} hemin standard solution.

respectively, as can be seen in Fig. 2. So DCQ has been proposed as the main reaction product for the oxidative dehalogenation of TCP (1). DCQ can undergo self-degradation by photoreactions [20,23,28,29], which may considerably help the oxidation of TCP, and it is less hazardous than TCP, so it does not appear in any contaminant list. Similar results were obtained when the reaction was carried out in 0.01 M acetate buffer pH 5.0 (data not shown).



(1)

Besides, the presence of chloride ions in solution was demonstrated with the thiocyanate method as a red complex was formed after the addition of $Hg(SCN)_2$ in the presence of Fe (III). No oxidation occurs in solutions containing TCP and H_2O_2 in the absence of the polymer (blank assays). The reaction reported in this work is very similar to the oxidative dehalogenation of TCP catalyzed by CPO, whose mechanism has been recently elucidated [30,31].

3.2.2. pH

Reaction (1) was carried out for 5 min with H_2O_2 10^{-3} M, TCP 10^{-5} M and different sodium acetate buffer solutions 0.01 M with pH values from 2.5 to 6.0 and the resulting DCQ was measured. Fig. 3 shows the pH profile with two relative optimal pH values (3.0 and 5.0). A similar behaviour has been reported for 2,4-DCP peroxidation catalyzed by CPO [9]. However, the highest amount of DCQ was obtained at pH 3.0, so this pH value was used for subsequent studies.

3.3. Kinetic study of the degradation of TCP with the acrylic polymer as catalyst

The time-course of DCQ formation and TCP utilization was obtained and the results are shown in Fig. 4. The amount of the

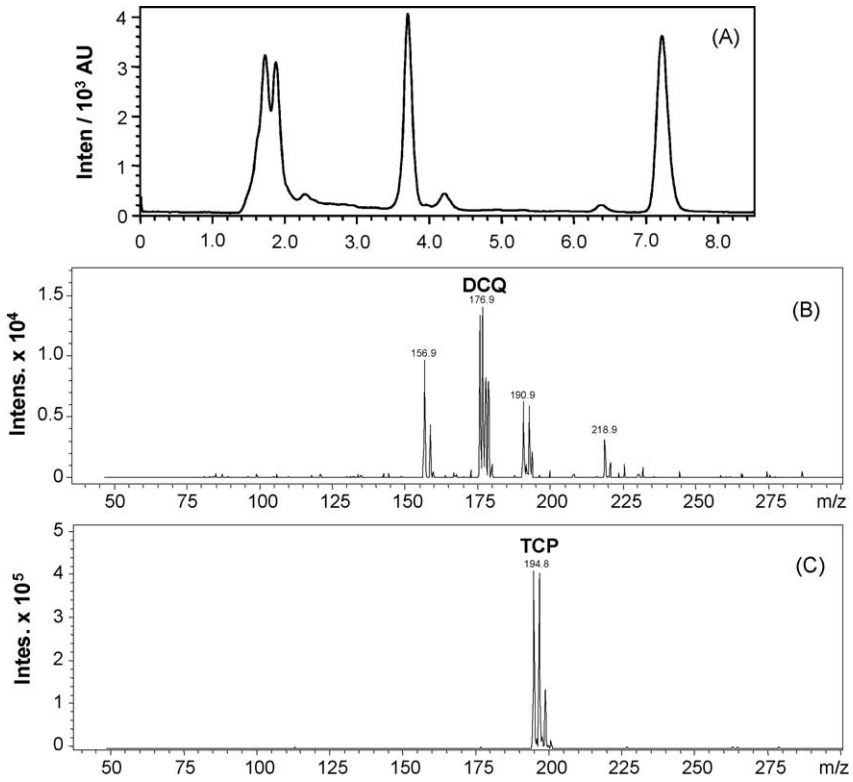


Fig. 2. (A) HPLC–VIS/UV (280 nm) chromatogram of the reaction medium after 5 min of reaction, and mass spectra of the reaction medium acquired at (B) 3.7 min (DCQ, $m/z = 176$) and (C) 7.2 min (TCP, $m/z = 194$). Reaction conditions: 0.5 g L^{-1} polymer, 10^{-3} M TCP, 10^{-3} M H_2O_2, reaction medium: acetate 0.01 M pH 3.0 with 10% DMSO.

DCQ generated in the reaction medium increases reaching a plateau after 15 min, while a decrease was observed on the concentration of TCP. We can also conclude from this figure that the time to degrade a 20 mg L^{-1} (~100 μM) TCP solution to non-detectable levels is 30 min (the limit of detection for the UV–VIS methodology was 10^{-6} M = 0.2 mg L^{-1}).

Steady-state rate of the reaction was estimated by measuring the concentration of the generated DCQ at a fixed reaction time of 2 min. A sigmoid dependence of initial rate upon TCP concentration was observed (Fig. 5). This curve was adjusted to the Hill equation with an iteration procedure following Marquardt–Levenberg non-linear least squares algorithm using Origin 8.1 software in order to obtain the values of the kinetic parameters. Values of $v_{max} = (2.4 \pm 0.2) \times 10^{-6}$ mol L^{-1} min^{-1}, the pseudo-Michaelis constant $K_s^* = (9 \pm 1) \times 10^{-5}$ M (~20 mg L^{-1}) and the Hill parameter $h = 2.0 \pm 0.4$ were obtained. This result could be explained by means of multiplicity of TCP binding within a large active site, in such a way that the binding of one TCP molecule to the acrylic polymer facilitates the

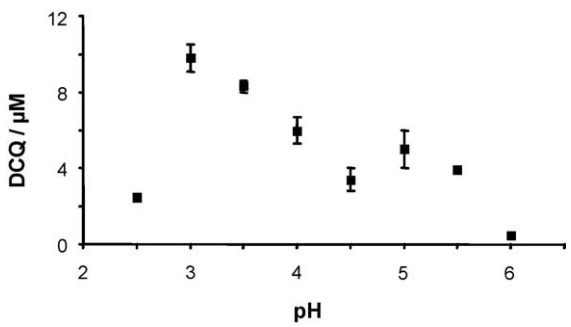


Fig. 3. DCQ concentration (μM) measured in the reaction medium at various pH values. Reaction conditions: 0.5 g L^{-1} polymer, 10^{-3} M H_2O_2, 10^{-5} M TCP, reaction medium: 0.01 M buffer with 10% DMSO, incubation time: 5 min.

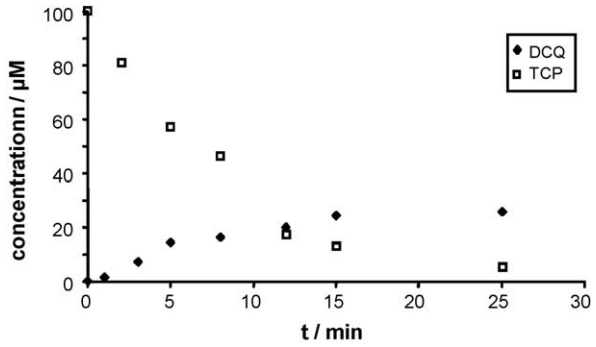


Fig. 4. Variation of TCP and DCQ concentrations with increasing reaction time. Reaction conditions: 0.5 g L^{-1} polymer, 10^{-3} M H_2O_2, 10^{-4} M TCP, reaction medium: 0.01 M acetate buffer pH 3.0 with 10% DMSO.

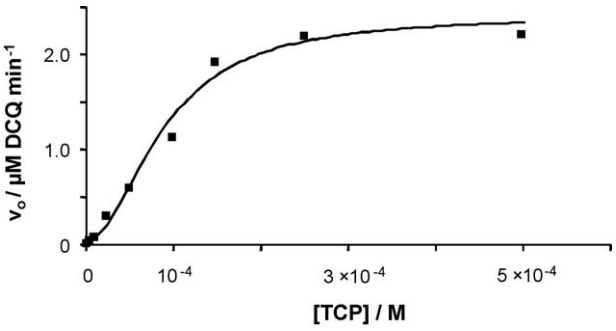


Fig. 5. Initial reaction rate at different TCP concentrations. Reaction conditions: 0.5 g L^{-1} polymer, 10^{-3} M H_2O_2, reaction medium: 0.01 M acetate buffer pH 3.0 with 10% DMSO, incubation time: 1 min. Fitted curve was obtained using Hill equation.

Table 3
Degradation strategies with microorganisms.

Degradation agent	Substrate	Initial concentration	Final concentration	Time	Reference
Bacterial culture	TCP	30 mg L^{-1}	n.d.	3 days	[4]
Phanerochaete chrysosporium	TCP	45 mg L^{-1}	25 mg L^{-1}	15 days	[4]
Sewage	TCP	40, 20, 10 mg L^{-1}	n.d.	3 days	[32]
Pseudomonas fluorescens, Cepacia methylobacter	Phenolic compounds	10 ppm	n.d.	48 h	[33]
Rhodococus mycobacterium	PCP	30 g L^{-1}	n.d.	–	[34]

n.d.: not detected.

successive TCP bindings, so cooperative effects may help TCP to degrade in the optimum conditions. The pseudo-Michaelis constant is similar to the value obtained for fungus *Phanerochaete chrysosporium* [4] in comparable pH conditions.

3.4. Other by-products

Apart from DCQ and TCP, other by-products were identified by MS spectrometry and HPLC/UV-VIS. In the chromatogram of the reaction medium (Fig. 2A) three more aromatic species appear at 2.3 min (λ_{max} = 260 nm), 4.2 min (λ_{max} = 276 nm) and 6.4 min (λ_{max} = 260–280 nm). The first one shows the following ions: *m/z* (relative intensity, 100) 418.9, *m/z* (67) 462.9 and *m/z* (17) 265. The second one exhibits *m/z* (100) 239 and *m/z* (52) 222.9. The last one shows seven ions with *m/z* (100) 378.9, *m/z* (56) 113.1, *m/z* (22) 226.8, *m/z* (89) 249.1, *m/z* (22) 264.8, *m/z* (33) 290.9 and *m/z* (11) 328.8. These unidentified products may be resulting from the coupling of phenoxy radicals but their structures have not been elucidated.

The time program used in HPLC measurements keeps an unresolved area before the peak of DCQ (unresolved in Fig. 2A), where we have found a species that has been characterized before [12,16] regarding its *m/z* ratio (141). It corresponds to a Cl atom loss from DCQ, but it has not been previously assigned to a certain structure. In addition, other product with *m/z* = 304.9 was detected and two possible structures (Fig. 6, structures 1 and 2) were proposed for it. Both of them correspond to species previously observed for TCP degradation with LiP [12] and a non-heme iron (III) complex [24].

Finally, an additional product was observed when we inject the washing methanol in the HPLC–MS. A *m/z* = 339.1 product was detected in the unresolved area and its structure has been elucidated by Hemmert et al. [24] (Fig. 6, structure 3).

3.5. Efficiency of the degradation process

Table 3 shows times required for other degradation methods found in the literature and leads to the conclusion that the acrylic polymer synthesized in this work is more efficient than the bacterial cultures because it allows almost completely TCP removal (20 mg L^{-1}) in a brief period of time (~30 min) compared to 3 or even 15 days in bacterial treatments. Besides, the acrylic polymer does not require an acclimatization process with nutrients because of its synthetic origin. This is an important feature because this step can last several moths and in some cases gives rise to the poisoning of microorganisms. Additional advantages of this synthetic material are the simplicity of its preparation, its low cost (approximately 0.67 €/g) and the use of an environmentally friendly oxidant (H_2O_2).

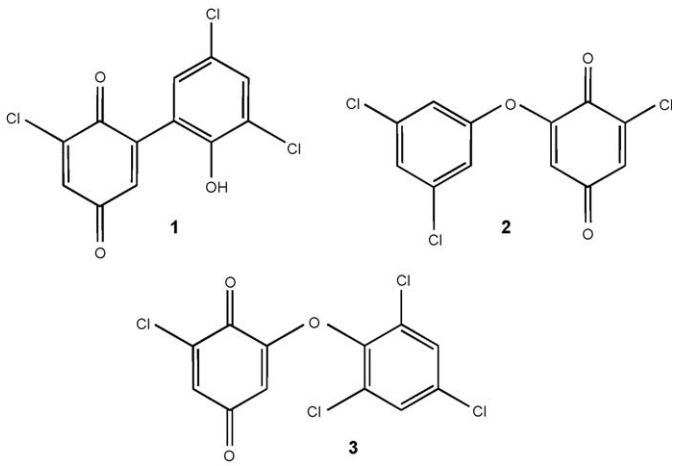


Fig. 6. Proposed structures for the products corresponding to *m/z* 304.9 and 339.1.

4. Conclusions

We have synthesized an acrylic polymer with capacity to catalyze the oxidative dehalogenation of TCP in solution, which exhibits faster kinetic behaviour than conventional methods. A solution of 20 mg L^{-1} can be degraded to not detectable levels in approximately 30 min. This novel material is easy to prepare and to incorporate in a low cost degradation process, which can be considered a highly competitive bioremediation route.

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